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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF  
HARVARD COLLEGE.

ON THE 3, 4, 5 TRIBROMANILINE AND SOME DERIVATIVES OF UNSYMMETRICAL TRIBROMBENZOL.

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Presented May 12, 1897.

IN the course of an attempt to prepare the vicinal tetrabrombenzol, which unfortunately did not lead to the desired result, we had occasion to make the 3, 4, 5 tribromaniline, when to our surprise our product melted at  $118^{\circ}$  to  $119^{\circ}$ , whereas Koerner, who discovered the substance, says of it, "non fondente a  $130^{\circ}$ , e che, a quanto pare, si scompone per un più forte riscaldamento."\* As the statement quoted from Koerner contained all that was known of the properties of the substance, except that he says also that it forms salts, we have made a more careful study of this tribromaniline in order to characterize it. Our melting point not only differed from Koerner's, but also was essentially identical with that of the ordinary tribromaniline  $\text{NH}_2\text{I}$ ,  $\text{Br}_3$  2, 4, 6, — which melts at  $118^{\circ}$  according to Koerner, at  $119^{\circ}$ – $120^{\circ}$  according to Fittig and Buchner. It was necessary, therefore, in the first place to prove that our substance was the tribromaniline  $\text{NH}_2\text{I}$ ,  $\text{Br}_3$  3, 4, 5, even although from our knowledge of the positions usually taken by bromine atoms on the benzol ring it seemed hardly possible that a body formed by the action of bromine on paranitraniline could have a different constitution. To make the proof absolute we eliminated the amido group from our tribromaniline, when we found that the vicinal tribrombenzol melting at  $87^{\circ}$  and crystallizing in tables was formed with remarkable ease. It follows, therefore, that Koerner's statement that the tribromaniline ( $\text{NH}_2\text{I}$ ,  $\text{Br}_3$  3, 4, 5) does not melt even at  $130^{\circ}$  is incorrect, and that it melts at  $118^{\circ}$ – $119^{\circ}$ . We have added to the description of the compounds of this tribromaniline which follows an account of some other substances obtained in our

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\* Gazz. Chim., 1874, p. 409.

attempts to make vicinal tetrabrombenzol, and also a few corrections and additions to our paper on "On Some Derivatives of Unsymmetrical Tribrombenzol" \* published somewhat more than a year ago.

3, 4, 5 TRIBROMANILINE,  $C_6H_2Br_3NH_2$ .

To prepare this substance † paranitraniline was suspended in water, and converted by the addition of bromine into dibromparanitraniline. Then fifty grams of this product were mixed in a flask with hydrobromic acid (boiling at  $125^\circ$ ), and sodic nitrite added in excess. After the last portion of the nitrite had been decomposed, a large excess of hydrobromic acid was added, and the contents of the flask allowed to stand over night. The diazo compound formed was then decomposed by heating on the steam bath; and the tribromnitrobenzol obtained was reduced with tin and hydrochloric acid without any previous purification, when most of the tribromaniline separated in the solid state, although a small amount could be recovered from the hydrochloric acid solution. It was purified by crystallization from alcohol or hot ligroin.

*Properties.* — It crystallizes from alcohol and water in slender white needles, rather short and pointed at both ends. Although it crystallizes in needles like the ordinary tribromaniline, it differs from that in habit, as we could not succeed in obtaining very long needles similar to those which are so characteristic of the  $NH_2$  1, Br 2, Br 4, Br 6 isomere. It melts between  $118^\circ$  and  $119^\circ$ , while the highest melting point given for the isomeric form is that of Fittig and Buchner,  $119^\circ$ – $120^\circ$ . It is soluble in ether, chloroform, benzol, acetone, or alcohol; slightly soluble in cold, soluble in hot ligroin; essentially insoluble in water. Dilute alcohol or hot ligroin is the best solvent for it. It forms salts more readily than the  $NH_2$  1, Br<sub>3</sub> 2, 4, 6 tribromaniline, and a little less readily than the  $NH_2$  1, Br<sub>3</sub> 2, 4, 5 tribromaniline.‡ With bromine it gives pentabromaniline. By the elimination of its amido group it is converted into the vicinal tribrombenzol melting at  $87^\circ$ .

CHLORIDE OF TRIBROMANILINE,  $NH_2$  1, Br<sub>3</sub> 3, 4, 5.

This salt could be made by boiling the tribromaniline with a large excess of concentrated hydrochloric acid, but was prepared for analysis by the more convenient method of dissolving the tribromaniline in benzol

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\* Amer. Chem. Journ., XVIII. 238.

† Koerner, Gazz. Chim., 1874, pp. 347, 390.

‡ Amer. Chem. Journ., XVIII. 247.

and adding a strong solution of hydrochloric acid \* when the salt was precipitated.

0.4976 gram of the salt gave, after the base had been removed by ammoniac hydrate, 0.1911 gram of argentic chloride.

	Calculated for $C_6H_2Br_3NH_2Cl$ .	Found.
Chlorine	9.69	9.50

*Properties.* — The salt crystallizes unaltered in white needles from hot water to which a few drops of hydrochloric acid have been added; but if it is boiled with water alone, it undergoes a partial decomposition. This salt is, therefore, much more stable than the chloride of the  $NH_2$  1,  $Br_3$  2, 4, 6 tribromaniline, which is decomposed completely by water. It is slightly soluble in benzol; insoluble in ligroin or ether.

#### BROMIDE OF TRIBROMANILINE, $NH_2$ 1, $Br_3$ 3, 4, 5.

This salt was made by adding a strong aqueous solution of hydrobromic acid to two grams of the tribromaniline dissolved in benzol. The white precipitate formed was filtered out, washed with benzol, dried, and analyzed with the following result: —

0.3841 gram of the salt gave, after the base had been precipitated with ammoniac hydrate, 0.1771 gram of argentic bromide.

	Calculated for $C_6H_2Br_3NH_2Br$ .	Found.
Bromine	19.47	19.63

The bromide resembles the chloride in its properties, and, although slightly more unstable, is still much more stable than the bromide of the tribromaniline  $NH_2$  1,  $Br_3$  2, 4, 6.

#### SULPHATE OF TRIBROMANILINE $NH_2$ 1, $Br_3$ 3, 4, 5.

To prepare this salt three grams of the tribromaniline were heated with moderately strong sulphuric acid. The tribromaniline soon dissolved, and on cooling the solution deposited fine large plates of the sulphate, which were purified by recrystallization from water slightly acidified with sulphuric acid, dried, and analyzed with the following result: —

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\* In order to obtain the chloride of the  $NH_2$  1,  $Br_3$  2, 4, 6 tribromaniline, gaseous hydrochloric acid must be used.

0.4671 gram of the substance, after treatment with ammoniac hydrate, gave 0.1417 gram of baric sulphate.

	Calculated for $(C_6H_2Br_3NH_2)_2H_2SO_4$ .	Found.
$SO_4$	12.66	12.49

*Properties.* — The salt crystallizes from dilute sulphuric acid in broad white shining plates, which are soluble in water; but if its aqueous solution is heated, it decomposes partially into the tribromaniline and sulphuric acid. In the presence of a little sulphuric acid, on the other hand, the aqueous solution can be heated without decomposition. The salt is soluble in alcohol, and its solubility is increased by heat; insoluble in benzol, chloroform, or ether.

TRIBROMOPHENYLURETHANE,  $C_6H_2Br_3NHCOOC_2H_5$ , NH 1, Br<sub>3</sub> 3, 4, 5.

This substance was prepared by boiling a benzol solution of ten grams of the tribromaniline with eight grams of chlorocarbonic ethyl ester in a flask with a return condenser. After heating for five hours, as no more hydrochloric acid was given off, the mixture was allowed to cool, when crystals appeared, which were filtered out, and crystallized from dilute alcohol until they showed the constant melting point  $169^\circ$ – $170^\circ$ . The substance was then dried at  $100^\circ$ , and analyzed with the following results: —

- I. 0.915 gram of the substance gave 0.2708 gram of argentic bromide by the method of Carius.
- II. 0.1771 gram of the substance gave 0.2473 gram of argentic bromide by the method of Carius.

	Calculated for $C_6H_2Br_3NHCOOC_2H_5$ .	Found.	
		I.	II.
Bromine	59.70	60.20	59.43

The  $NH_2$  1, Br<sub>3</sub> 2, 4, 6 tribromaniline gives no urethane under these conditions.

*Properties.* — This tribromophenylurethane crystallizes from a mixture of alcohol and water in thin white rhombic plates frequently with the acute angles bevelled by two other planes making a very obtuse angle with the sides of the original rhomb. It melts at  $169^\circ$ – $170^\circ$ ; and is easily soluble in alcohol, ether, benzol, or chloroform; essentially insoluble in cold ligroin, soluble in hot. Strong hydrochloric acid in the cold has no apparent action on it. Strong nitric acid or strong sulphuric

acid dissolves it, and the addition of water to the solution gives a white precipitate.

When the tribromophenylurethane was boiled with aniline under a reverse condenser, a substance was obtained, after removing the excess of aniline with dilute hydrochloric acid, which crystallized from alcohol in very long needles, melted at  $235^{\circ}$ , and contained no halogen. There was no doubt, therefore, that it was diphenylurea  $(\text{C}_6\text{H}_5\text{NH})_2\text{CO}$ , and that the aniline had replaced both the ethoxy group of the ester and the tribromophenylimido group by phenylimido radicals.

TRIBROMACETANILID,  $\text{C}_6\text{H}_2\text{Br}_3\text{NHCOCH}_3$ , NH 1, Br<sub>3</sub> 3, 4, 5.

Eight grams of the perfectly dry tribromaniline were mixed in small portions at a time with a large excess of acetic anhydride, and the dark colored solution warmed on the steam bath for a few minutes. The substance was then precipitated by pouring its solution into water, and purified by many recrystallizations from alcohol, after which it was dried at  $100^{\circ}$ , and analyzed with the following results:—

- I. 0.1817 gram of the substance gave 0.2756 gram of argentic bromide by the method of Carius.
- II. 0.1114 gram of the substance gave 0.1691 gram of argentic bromide.

	Calculated for $\text{C}_6\text{H}_2\text{Br}_3\text{NHCOCH}_3$ .	Found.	
		I.	II.
Bromine	64.50	64.55	64.63

*Properties.*—This tribromacetanilid crystallizes from alcohol in white slightly radiating brushes made up of very small needles, or in globular groups of needles looking like chestnut burs. It melts at  $253^{\circ}$ – $254^{\circ}$ . The tribromacetanilid NH 1, Br<sub>3</sub> 2, 4, 6 melts at  $232^{\circ}$  according to Remmers. Our acetanilid is soluble in benzol, and in hot alcohol, but only slightly soluble in cold alcohol; soluble with difficulty in ether or chloroform; essentially insoluble in ligroin. Sulphuric acid saponifies it only after long boiling. Fuming nitric acid converts it into the nitro compound described below.

TRIBROMNITROACETANILID,  $\text{C}_6\text{HBr}_3\text{NO}_2\text{NHCOCH}_3$ ,  
NH 1, Br<sub>3</sub> 3, 4, 5, NO<sub>2</sub> 2.

To prepare this substance twenty grams of the dry tribromacetanilid were added in small portions at a time to a quantity of nitric acid of specific gravity 1.50. As the reaction is vigorous, the flask must be

cooled and shaken continually during the addition of the acetanilid. The solution thus obtained was poured into water, and the yellowish precipitate crystallized from a mixture of acetone and alcohol until it showed the constant melting-point  $229^{\circ}$ , when it was dried at  $100^{\circ}$ , and analyzed with the following results: —

- I. 0.1485 gram of the substance gave 0.2009 gram of argentic bromide by the method of Carius.  
 II. 0.1624 gram of the substance gave 0.2194 gram of argentic bromide.

	Calculated for $C_6HBr_3NO_2NHCOCH_3$ .	Found.	
		I.	II.
Bromine	57.55	57.55	57.49

*Properties.* — This tribromnitracetanilid crystallizes from alcohol and acetone in white well formed crystals belonging either to the hexagonal or orthorhombic system. When less well crystallized it forms long very slender prisms terminated by a single plane at an oblique angle, or thick clumps of curving needles. It melts at  $229^{\circ}$ ; and is easily soluble in acetone; soluble in alcohol; slightly soluble in benzol or ether; essentially insoluble in ligroin. Sulphuric acid saponifies it in time, but this effect is produced much more easily by a strong solution of sodic hydrate.

TRIBROMNITRANILINE,  $C_6HBr_3NO_2NH_2$ ,  $NH_2$  1,  $Br_3$  3, 4, 5,  $NO_2$  2.

This substance was obtained by boiling ten grams of tribromnitracetanilid with a strong solution of sodic hydrate. As the tribromnitracetanilid was saponified, the solution took on a deep reddish brown color. When the reaction was complete, the solution was acidified with acetic acid, which threw down a brownish precipitate. This was filtered out, and recrystallized from alcohol and chloroform until it showed the constant melting point  $130^{\circ}$ , when it was dried at  $100^{\circ}$ , and analyzed with the following results: —

- I. 0.1912 gram of the substance gave 0.2864 gram of argentic bromide by the method of Carius.  
 II. 0.2006 gram of the substance gave 0.3017 gram of argentic bromide.  
 III. 0.2624 gram of the substance gave 18.1 c.c. of nitrogen at a temperature of  $19^{\circ}.4$  and a pressure of 761.2 mm.

	Calculated for $C_6HBr_3NO_2NH_2$ .	Found.		
		I.	II.	III.
Bromine	64.00	63.77	64.01	
Nitrogen	7.47			7.93

*Properties.* — This tribromnitriline crystallizes from alcohol in yellowish orange needles arranged in radiating groups. If the cooling is rapid, little circular masses of needles are formed. It melts at  $130^{\circ}$ ; and is easily soluble in alcohol, ether, benzol, or chloroform; essentially insoluble in ligroin, or in cold water, slightly soluble in boiling water.

In the hope of converting the tribromnitriline just described into a tribromnitrobenzol, from which the vicinal tetrabrombenzol might be obtained, we submitted it to the diazo reaction as follows. Fourteen grams of the tribromnitriline were dissolved in boiling alcohol previously acidified with sulphuric acid, and ten grams of powdered sodic nitrite added in small portions at a time. The mixture was then boiled for thirty minutes, and allowed to stand over night at ordinary temperatures. Upon adding water a yellowish precipitate was formed, which, after recrystallization from alcohol, melted at  $230^{\circ}$ . An analysis indicated that the substance was the phenol  $C_6HBr_3NO_2OH$ , although the agreement between the percentage of bromine found and that calculated left much to be desired. (Calculated per cent of bromine, 63.83. Found, 64.54.) Unfortunately, we did not have enough substance for more thorough purification; but its properties showed plainly that it was a phenol, as it dissolved in a solution of sodic ethylate forming a reddish brown salt, from which the original substance was recovered by acidification. As, therefore, this line of work evidently would not lead to the vicinal tetrabrombenzol, we did not think it worth while to undergo the large amount of labor necessary to prepare more of this phenol in order to characterize it more satisfactorily.

TRIBROMPHENYLURETHANE,  $C_6H_2Br_3NHCOOC_2H_5$ , NH 1, Br<sub>3</sub> 2, 4, 5.

This substance was prepared in order to characterize more fully the tribromaniline  $NH_2$ 1, Br<sub>3</sub> 2, 4, 5, described in our first paper.\* Ten grams of the tribromaniline dissolved in benzol were heated with eight grams of chlorocarbonic ethyl ester in a flask with a return condenser, until no more hydrochloric acid was given off. The product thus obtained was crystallized from alcohol, until it showed the constant melting point  $101^{\circ}$ , when it was dried, and analyzed with the following result:—

0.1432 gram of the substance gave 0.2016 gram of argentic bromide by the method of Carius.

	Calculated for $C_6H_2Br_3NHCOOC_2H_5$ .	Found.
Bromine	59.70	59.92

\* Amer. Chem. Journ., XVIII, 247.



*Properties.* — This tribromophenylurethane crystallizes from alcohol and water in long slender white needles in radiating bunches forming a thick felted mass. It melts at  $101^{\circ}$ ; and is freely soluble in alcohol, ether, benzol, chloroform, or glacial acetic acid; insoluble in water. When it is heated with aniline it yields diphenylurea melting at  $235^{\circ}$ , and the tribromaniline, which was recognized by its peculiar odor. Its behavior, therefore, in this respect is like that of the tribromophenylurethane NH 1, Br<sub>3</sub> 3, 4, 5, previously described in this paper.

TRIBROMNITRACETANILID,  $C_6HBr_3NO_2NHCOCCH_3$ , NH 1, Br<sub>3</sub> 2, 4, 5.

This substance was prepared from the corresponding acetanilid described in our previous paper.\* We have not determined the position of the nitro group, but should suppose it would be ortho to the acetamido group, and therefore 6. Five grams of the tribromacetanilid were added in small portions at a time to about forty grams of nitric acid of specific gravity 1.50. The mixture was allowed to stand an hour at ordinary temperatures, and then poured into a large volume of cold water; the precipitate was recrystallized from alcohol, until it showed the constant melting point  $228^{\circ}$ , when it was dried at  $100^{\circ}$ , and analyzed with the following result:—

0.1001 gram of the substance gave 0.1348 gram of argentic bromide by the method of Carius.

	Calculated for $C_6HBr_3NO_2NHCOCCH_3$ .	Found.
Bromine	57.55	57.33

*Properties.* — This tribromnitracetanilid crystallizes from hot alcohol in little branched needles generally arranged in circular radiating groups, or in sheaves. It was pinkish white, but is probably white when perfectly pure. It melts at  $228^{\circ}$ ; and is freely soluble in ether, benzol, chloroform, carbonic disulphide, or glacial acetic acid. Sulphuric acid, when boiled with it, converts it into the tribromnitriline described below.

TRIBROMNITRANILINE,  $C_6HBr_3NO_2NH_2$ , NH<sub>2</sub> 1, Br<sub>3</sub> 2, 4, 5.

Ten grams of the tribromnitracetanilid were heated in a flask with a return condenser with sulphuric acid diluted to the specific gravity 1.44, until the solid went into solution. The solution after it had cooled was diluted with water, neutralized with dilute sodic hydrate, and the brownish precipitate purified by recrystallization from alcohol. When it showed

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\* Amer. Chem. Journ., XVIII. 249.

the constant melting point  $130^{\circ}$ , the substance was dried at  $100^{\circ}$ , and analyzed with the following result:—

0.2341 gram of the substance gave 0.3513 gram of argentic bromide by the method of Carius.

	Calculated for $C_6HBr_3NO_2NH_2$ .	Found.
Bromine	64.00	63.87

*Properties.*— This tribromnitraniline crystallizes in rather thick yellow needles often united longitudinally, and sometimes very much branched. It melts at  $130^{\circ}$ ; and is very soluble in ether, benzol, chloroform, acetone, ligroin, or carbonic disulphide; soluble in alcohol; soluble with difficulty in hot water.

BEHAVIOR OF TRIBROMDINITROBENZOL ( $Br_3$  1, 2, 4 ( $NO_2$ )<sub>2</sub> 3, 5)  
WITH SODIC ETHYLATE.

This reaction was described in our previous paper,\* but, unfortunately, in determining the composition of the principal product we relied only on a bromine determination. On returning to the subject we realized that this was entirely insufficient to settle the nature of the body, since the ethoxy group has nearly the same molecular weight, 45, as the nitro group, 46, and therefore our bromine determination would serve equally well for a tribromresorcine (the composition which we had assigned to it, percentage of bromine 59.55), or for a tribromnitrophenetol (percentage of bromine 59.40). We accordingly prepared some more of the substance and tested for nitrogen, when to our great mortification we found that it was present, and that the substance therefore is tribromnitrophenetol, and not tribromresorcine. We regret exceedingly that our carelessness should have introduced this mistake into the chemical literature. Its composition was definitely settled by the following analyses:—

- I. 0.2430 gram of the substance gave 0.3407 gram of argentic bromide by the method of Carius.
- II. 0.3797 gram of the substance gave 11.9 c.c. of nitrogen at a temperature of  $26^{\circ}$  and a pressure of 766.5 mm.

	Calculated for $C_6HBr_3NO_2OC_2H_5$	Found.	
		I.	II.
Bromine	59.40	59.67	
Nitrogen	3.47		3.51

\* Amer. Chem. Journ., XVIII. 244.

*Properties of Tribromnitrophenetol.*—These were given in our first paper as the properties of tribromresorcine; we therefore think it best to repeat them here under the true name. It crystallizes from alcohol in long white pearly plates terminated by two planes at an acute angle, which is usually truncated by a basal plane. It melts at  $158^{\circ}$ . It is nearly insoluble in cold alcohol, soluble in hot; soluble in chloroform, benzol, or acetone; slightly soluble in cold ligroin, more soluble in hot. The best solvent for it is hot alcohol.

In the aqueous filtrate from the tribromnitrophenetol we found the salt of a diatomic phenol melting at  $67^{\circ}$ , to which in our previous paper we assigned the formula  $C_6HBr(NO_2)_2(OH)_2$ , on the ground of a bromine determination. In returning to the subject we thought it well to obtain more analytical data in regard to it, and for this purpose we have made and analyzed the barium salt.

BARIUM SALT OF BROMDINITRORESORCINE(?),  $C_6HBr(NO_2)_2O_2Ba$ .

The constitution of the phenol has not been proved; but, as according to analogy the two hydroxyls should be in the meta position to each other, we have adopted the name given above provisionally.

The barium salt was prepared as follows. Two grams of the phenol were mixed with a freshly prepared alcoholic solution of sodic ethylate, and then treated with an aqueous solution of baric chloride. The yellow precipitate thus obtained was filtered as quickly as possible, washed three times with a little cold water, and once with ether, and then dried at  $130^{\circ}$ , and analyzed with the following result:—

0.2580 gram of the salt gave 0.1464 gram of baric sulphate.

	Calculated for $C_6HBr(NO_2)_2O_2Ba$ .	Found.
Barium	33.09	33.36

This analysis, therefore, confirms our previous view of the composition of the phenol.

*Properties.*—The barium salt is an orange-yellow powder with no well defined crystalline form. When heated in the flame of a Bunsen lamp, it explodes. It is soluble in water, and its solubility is increased by heat; slightly soluble in alcohol; insoluble in ether, chloroform, or ligroin. Acids set free the phenol  $C_6HBr(NO_2)_2(OH)_2$  from it.